PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-077573

(43)Date of publication of application : 25.03.1997

(51)Int.Cl.	C04B 38/06
	B01D 39/20
	B01J 21/16
	B01J 35/04
	C04B 35/195
	F01N 3/02
	// B01D 46/00

(21)Application number : 08-175864	(71)Applicant : DENSO CORP
(22)Date of filing : 14.06.1996	(72)Inventor : KONDO TOSHIHARU
	ITO KEIJI
	KAGEYAMA TERUTAKA
	OBATA TAKASHI

(30)Priority

Priority number : 07200424   Priority date : 12.07.1995   Priority country : JP

(54) HONEYCOMB STRUCTURE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a cordierite honeycomb structure having such characteristics as a high rate of capture, a small pressure drop and a low coefft. of thermal expansion.

SOLUTION: This honeycomb structure is based on cordierite having a chemical structure consisting of 45-55wt.% SiO2, 33-42wt.% Al2O3, and 12-18wt.% MgO and has ≤0.3×10-6/°C coefft. of thermal expansion in the range of 25-800°C, 55-80% porosity and 25-40μm average pore diameter. The pores in the surfaces of the partition walls are fine pores of 5-40μm and coarse pores of 40-100μm and the number of the fine pores is 5-40 times that of the coarse pores.

LEGAL STATUS

[Date of request for examination]	04.07.2002
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3806975
[Date of registration]	26.05.2006
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] It is the honeycomb structure object which uses as a principal component cordierite which chemical composition becomes from 12 - 18 % of the weight of MgO(s) SiO2 45-55 % of the weight and aluminum2 O3 33-42% of the weight. Among 25-800 degrees C Less than [0.3x10-6/degree C] and porosity are [55 - 80% and an average pole diameter] 25-40 micrometers, and the pore on the front face of a septum consists of a 5-40 micrometers stoma and a 40-100-micrometer osculum, and the coefficient of thermal expansion which can be set that the number of the above-mentioned stomata is 5 to 40 times the number of the above-mentioned osculums The honeycomb structure object by which it is characterized.
[Claim 2] It is the honeycomb structure object characterized by the above-mentioned porosity being 62 - 75% in claim 1.
[Claim 3] Chemical composition uses as a principal component cordierite which consists of 12 - 18 % of the weight of MgO(s) SiO2 45-55 % of the weight and aluminum2 O3 33-42% of the weight. Among 25-800 degrees C Less than [0.3x10-6/degree C] and porosity are [55 - 80% and an average pole diameter] 25-40 micrometers, and the pore on the front face of a septum consists of a 5-40 micrometers stoma and a 40-100-micrometer osculum, and the coefficient of thermal expansion which can be set the honeycomb structure object whose number of the above-mentioned stomata is 5 to 40 times the number of the above-mentioned osculums It is the approach of manufacturing and is Fe 2O3. Talc whose sum total content of 0.1 - 0.6 % of the weight, CaO, Na2 O, and K2 O a content is 0.35 or less % of the weight, While the large drop child the granule child whose particle diameter is 0.5-3 micrometers, and whose particle diameter are 5-15 micrometers occupies 50 - 100% of the weight of the whole The aluminum hydroxide whose weight-mix ratio of the above-mentioned large drop child to the above-mentioned granule child is within the limits of 5 / 95 - 95/5, Mean particle diameter 30-100 micrometers, Na2 O, and K2 The sum total content of O 0.01 or less % of the weight of fused silica When it uses and the mixture of the above-mentioned talc, the above-mentioned aluminum hydroxide, and the above-mentioned fused silica is calcinated, so that chemical composition may serve as 12 - 18 % of the weight of MgO(s) SiO2 45-55 % of the weight and aluminum2 O3 33-42% of the weight Mix the above-mentioned talc, the above-mentioned aluminum hydroxide, and the above-mentioned fused silica, consider as basic raw materials, and these basic raw materials are received. The manufacture approach of the honeycomb structure object characterized by adding the organic blowing agent to which it foams below 100 degrees C, or the combustible material which burns at temperature lower than burning temperature a total of five to 50% of the weight, kneading it, drying after fabricating in a honeycomb configuration subsequently, and subsequently calcinating.
[Claim 4] Fe 2O3 contained in the above-mentioned basic raw materials in claim 3 An amount is the manufacture approach of the honeycomb structure object characterized by being 0.7 or less % of the weight.
[Claim 5] It is the manufacture approach of the honeycomb structure object characterized by the above-mentioned combustible material being carbon in claim 3 or 4.
[Claim 6] The sum total weight of the above-mentioned [set in any 1 term of claims 3-5, and] talc in the above-mentioned basic raw materials, the above-mentioned aluminum hydroxide, and the above-mentioned fused silica is the manufacture approach of the honeycomb structure object characterized by occupying 80% or more.
[Claim 7] It is the manufacture approach of the honeycomb structure object characterized by the above-mentioned large drop child's weight-mix ratio to the above-mentioned granule child in the above-mentioned aluminum hydroxide being within the limits of 5 / 95 - 50/50 in any 1 term of claims 3-6.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the honeycomb structure object and its manufacture approach made from the cordierite which uses the particulate discharged by the Diesel engine for the filter which carries out uptake.
[0002]
[Description of the Prior Art] In order to carry out uptake of the particulate discharged by the Diesel engine, the filter which used the honeycomb structure object made from cordierite is used. As shown in drawing 5 and drawing 6 , the conventional honeycomb structure object 90 is a cylindrical shape-like, and has many the introductory paths 2 and the blowdown paths 3 which were established in the longitudinal direction.
[0003] As shown in drawing 5 and drawing 6 , the introductory path 2 is carrying out opening of the emission gas installation side, and, on the other hand, has blockaded the blowdown side by the lock out material 42. Moreover, the blowdown path 3 has blockaded the emission gas installation side by the lock out material 43, and, on the other hand, has carried out opening of the blowdown side. And as it is indicated in drawing 5 and drawing 6 as the introductory path 2 and the blowdown path 3, it arranges in the shape of [so-called] a checker by turns in the lengthwise direction and the longitudinal direction. Moreover, the septum 5 which constitutes the above-mentioned introductory path 2 and the blowdown path 3 is porosity, and has much pores.
[0004] Next, in case uptake of the particulate is carried out with the filter using the above-mentioned conventional honeycomb structure object 90, as shown in drawing 6 , the emission gas which contained the particulate first advances into the above-mentioned introductory path 2. Subsequently, since the blowdown side of the above-mentioned introductory path 2 is blockaded, the emission gas which has advanced passes a septum 5 and advances into the above-mentioned blowdown path 3. At this time, the above-mentioned septum 5 captures the particulate in emission gas, and purifies emission gas. Subsequently, the purified emission gas is discharged from the opening edge of the blowdown path 3.
[0005] In the filter using such a honeycomb structure object, the property of low voltage loss and low coefficient of thermal expansion is demanded besides the property which carries out uptake of the particulate with high collection efficiency. That is, there are the three above-mentioned demand characteristics as an important property especially. On the other hand, the honeycomb structure object shown in JP,5-254958,A is one of those aimed at low coefficient-of-thermal-expansion-ization.
[0006]
[Problem(s) to be Solved] However, there is the following trouble in the above-mentioned conventional honeycomb structure object. That is, since the honeycomb structure object shown in the above-mentioned official report is low coefficient of thermal expansion, it is excellent in thermal shock resistance, and it is good. [of collection efficiency] However, since porosity is low, a pressure loss cannot be stopped low.
[0007] Moreover, in the other conventional honeycomb structure objects, there is nothing that fills all of the three above-mentioned demand characteristics, and although any two demand characteristics are satisfied, remaining one demand characteristics are not satisfied. This invention was made in view of this conventional trouble, and tends to offer the honeycomb structure object having the property of high collection efficiency, low voltage loss, and low coefficient of thermal expansion, and its manufacture approach.
[0008]
[Means for Solving the Problem] Invention of claim 1 is a honeycomb structure object which uses as a principal component cordierite which chemical composition becomes from 12 - 18 % of the weight of MgO(s) SiO2 45-55 % of the weight and aluminum2 O3 33-42% of the weight. Among 25-800 degrees C Less than [0.3x10-6/degree C] and porosity are [55 - 80% and an average pole diameter] 25-40 micrometers, and the pore on the front face of a septum consists of a 5-40 micrometers stoma and a 40-100-micrometer osculum, and the coefficient of thermal expansion which can be set that the number of the above-mentioned stomata is 5 to 40 times the number of the above-mentioned osculums It is in the honeycomb structure object by which it is characterized.
[0009] For the above-mentioned coefficient of thermal expansion, less than [0.3x10-6/degree C] and porosity are [55 - 80% and the average pole diameter of what should be most observed in this invention] 25-40 micrometers, and the pore on the front face of a septum is that the number of the above-mentioned stomata is 5 to 40 times the number of the above-mentioned osculums.
[0010] When the above-mentioned coefficient of thermal expansion exceeds 0.3x10-6/degree C, there is a problem that thermal shock resistance gets worse.
[0011] Moreover, when the above-mentioned porosity is less than 55%, there is a problem that a pressure loss becomes high and it is still more preferably [62% or more of] good. On the other hand, there is a problem that collection efficiency falls in exceeding 80%, and it is still more preferably [75% or less of] good. That is, as for the above-mentioned porosity, it is still more desirable like invention of claim 2 that it is 62 - 75%.
[0012] Moreover, when the above-mentioned average pole diameter is less than 25 micrometers, there is a problem that a pressure loss becomes high, and on the other hand, in exceeding 40 micrometers, there is a problem that collection efficiency falls. Moreover, in the pore on the above-mentioned front face of a septum, when the number of osculums has few above-mentioned stomata than 5 times, the collection efficiency of the first stage at the time of uptake initiation is inferior. On the other hand, in exceeding 40 times, while the whole collection efficiency falls, there is a problem that product reinforcement falls. In addition, the detail of the reason is as having indicated to JP,61-129015,A.
[0013] Moreover, the above-mentioned honeycomb structure object can be made into the configuration which has the appearance of the shape for example, of a cylinder, and has the path of a large number formed by the septum for introducing and discharging emission gas to the longitudinal direction. The above-mentioned appearance can also be made into the configuration of a rectangular parallelepiped and others in addition to cylindrical. Moreover, although the cross-section configuration of the above-mentioned path is

the easiest to make it a square constitutionally, it is satisfactory even if it makes it a hexagon, a triangle, and other configurations.

[0014] Next, it explains per [in this invention] operation effectiveness. The coefficient of thermal expansion [object / of this invention / honeycomb structure] between 25-800 degrees C is less than [0.3x10-6/degree C]. Therefore, even if the dramatically excellent thermal shock resistance is shown and a rapid temperature change occurs repeatedly, it does not damage.

[0015] Moreover, porosity is 55 - 80%, and an average pole diameter is 25-40 micrometers, and the number of the above-mentioned stomata of the pore on the front face of a septum is 5 to 40 times the number of the above-mentioned osculums. Therefore, high collection efficiency and low voltage loss can be obtained.

[0016] That is, although a raise in porosity and major-diameter-izing of an average pole diameter are advantageous for the formation of low voltage disadvantage, in the configuration of this invention, this is fully satisfied. On the other hand, if raise in porosity and major-diameter-ization of an average pole diameter are advanced too much, usually collection efficiency will be reduced. However, in this invention, the rate of the stoma of the above-mentioned specific magnitude and osculum in the pore on the above-mentioned front face of a septum is regulated to specific within the limits. Therefore, even if it is high porosity and an average pole diameter is a major diameter, high collection efficiency is maintainable.

[0017] Therefore, according to this invention, the honeycomb structure object having the property of high collection efficiency, low voltage loss, and low coefficient of thermal expansion can be offered.

[0018] Next, there are the following approaches as an approach of manufacturing the above-mentioned honeycomb structure object. Chemical composition uses as a principal component cordierite which consists of 12 - 18 % of the weight of MgO(s) like invention of claim 3 SiO2 45-55 % of the weight and aluminum2 O3 33-42% of the weight. Namely, among 25-800 degrees C Less than [0.3x10-6/degree C] and porosity are [55 - 80% and an average pole diameter] 25-40 micrometers, and the pore on the front face of a septum consists of a 5-40 micrometers stoma and a 40-100-micrometer osculum, and the coefficient of thermal expansion which can be set the honeycomb structure object whose number of the above-mentioned stomata is 5 to 40 times the number of the above-mentioned osculums It is the approach of manufacturing and is Fe 2O3. Talc whose sum total content of 0.1 - 0.6 % of the weight, CaO, Na2 O, and K2 O a content is 0.35 or less % of the weight, While the large drop child the granule child whose particle diameter is 0.5-3 micrometers, and whose particle diameter are 5-15 micrometers occupies 50 - 100% of the weight of the whole The aluminum hydroxide whose weight-mix ratio of the above-mentioned large drop child to the above-mentioned granule child is within the limits of 5 / 95 - 95/5, Mean particle diameter 30-100 micrometers, Na2 O, and K2 The sum total content of O 0.01 or less % of the weight of fused silica When it uses and the mixture of the above-mentioned talc, the above-mentioned aluminum hydroxide, and the above-mentioned fused silica is calcinated, so that chemical composition may serve as 12 - 18 % of the weight of MgO(s) SiO2 45-55 % of the weight and aluminum2 O3 33-42% of the weight Mix the above-mentioned talc, the above-mentioned aluminum hydroxide, and the above-mentioned fused silica, consider as basic raw materials, and these basic raw materials are received. The organic blowing agent to which it foams below 100 degrees C, or the combustible material which burns at temperature lower than burning temperature is added a total of five to 50% of the weight, and is kneaded, subsequently, after fabricating in a honeycomb configuration, it dries and there is the manufacture approach of the honeycomb structure object characterized by subsequently calcinating.

[0019] What should be most observed in the above-mentioned manufacture approach is mixing the above-mentioned talc, the above-mentioned aluminum hydroxide, and the above-mentioned fused silica, and considering as basic raw materials. That is, it is not using clay and aluminas, such as a kaolin generally used as a raw material of cordierite, as basic raw materials. Moreover, it is adding the above-mentioned organic blowing agent or the above-mentioned combustible material in the above-mentioned specific range to basic raw materials.

[0020] Moreover, it sets to the above-mentioned talc and is Fe 2O3. When a content separates from the above-mentioned limited range, there are the following nonconformities. Namely, Fe 2O3 When a content is less than 0.1 % of the weight, there is a problem that the burning-temperature range for obtaining a low coefficient of thermal expansion becomes narrow. There is a problem that burn on the other hand while a coefficient of thermal expansion becomes large, in exceeding 0.6 % of the weight, and tightness is promoted, and high porosity-ization is barred. Moreover, when the sum total content of the impurity which consists of CaO, Na2 O, and K2 O exceeds 0.35 % of the weight, there is a problem that a coefficient of thermal expansion becomes high.

[0021] Moreover, as for the above-mentioned aluminum-hydroxide odor, the aluminum hydroxide of the granule child whose particle diameter is 0.5-3 micrometers, and the aluminum hydroxide of the large drop child whose particle diameter is 5-15 micrometers form 50 - 100% of the whole aluminum hydroxide. And when the thing of the above-mentioned granule child and the above-mentioned large drop child becomes less than 50%, it will become very difficult to obtain desired porosity and coefficient of thermal expansion. That is, as the particle size distribution of the aluminum hydroxide in this invention is shown in drawing 4 , it is characterized by more 0.5-3-micrometer particle charge's things and things with a particle diameter of 5-15 micrometers than the thing of other particle diameter existing.

[0022] Furthermore, when the weight-mix ratio of above-mentioned granule child's aluminum hydroxide and the above-mentioned large drop child's aluminum hydroxide is less than 5/95, reactivity falls, there is a problem that a coefficient of thermal expansion becomes large, and 5/95 or more is preferably good. On the other hand, in exceeding 95/5, the problem that pore volume is not made greatly arises. Therefore, in this invention, as for the above-mentioned weight-mix ratio, 5 / 95 - 95/5 are good, and it limits to this range. Furthermore, especially the range of 5 / 95 - 50/50 is desirable so that it may mention later.

[0023] Moreover, in the above-mentioned fused silica, when mean particle diameter is less than 30 micrometers, there is a problem that the number of the comparatively big holes prepared in a septum front face will decrease. On the other hand, in exceeding 100 micrometers, there is a problem of reducing the reinforcement of a honeycomb structure object. Moreover, when the sum total content of the impurity which consists of Na2 O contained in fused silica and K2 O exceeds 0.01 % of the weight, there is a problem that a coefficient of thermal expansion will become high.

[0024] Moreover, the organic blowing agent to which it foams below 100 degrees C, or the combustible material which burns at temperature lower than the above-mentioned burning temperature is added to the above-mentioned basic raw materials. The sum total addition of the above-mentioned organic blowing agent or combustible material is 5 - 50 % of the weight to basic raw materials. There is a problem that an average pole diameter becomes small too much in less than 5% of the weight of a case. On the other hand, in exceeding 50 % of the weight, there is a problem that an average pole diameter becomes large too much.

[0025] As the above-mentioned organic blowing agent, there is Matsumoto Yushi-Seiyaku micro staple fiber wear, for example. Moreover, the reason with required foaming below 100 degrees C is that it aims at making it foam in the above-mentioned desiccation process, and corresponds to whenever [stoving temperature / of a desiccation process].

[0026] Next, as the shaping approach to the honeycomb configuration of the above-mentioned basic raw materials, water etc. is added and kneaded, for example to the above-mentioned basic raw materials, and there is the approach of carrying out extrusion molding of this. According to this approach, the honeycomb Plastic solid of a request dimension can be easily acquired by cutting after extrusion molding in a honeycomb configuration.

[0027] Moreover, desiccation of the fabricated honeycomb Plastic solid is performed by [which carry out for accumulating, for example, heats at about 80-100 degrees C] evaporating the above-mentioned moisture etc. As for heating time, it is desirable to choose suitably according to the magnitude of a honeycomb Plastic solid etc. Moreover, baking can be performed by holding it in the temperature of about 1300-1500 degrees C for 5 to 20 hours as usual. However, as for burning temperature and time amount, it is desirable to change suitably with the magnitude of a honeycomb Plastic solid etc. In addition, although the above-mentioned desiccation process and a baking process may be performed as a separate process, they can also be summarized at one process by changing into burning temperature continuously from drying temperature.

[0028] Next, it explains per operation effectiveness of the above-mentioned manufacture approach. In the manufacture approach of the above-mentioned honeycomb structure object, it does not perform adding clay and aluminas, such as a kaolin, positively like before, using the above-mentioned talc, the above-mentioned aluminum hydroxide, and the above-mentioned fused silica as basic raw materials. Therefore, although the frame section with comparatively few holes was conventionally formed with clay and aluminas, such as a kaolin, in this invention, the frame section serves as porosity conventionally by fused silica or the aluminum hydroxide.

[0029] That is, by using an aluminum hydroxide, the water of crystallization contained in it evaporates, and many holes are formed. Moreover, fused silica is decomposed in a combustion process and the part becomes pore by the volumetric shrinkage in that case. So, porosity can be further made higher than before.

[0030] Moreover, in the above-mentioned aluminum hydroxide, the above-mentioned granule child mainly forms a 0.3-0.7-micrometer hole, and, on the other hand, the above-mentioned large drop child mainly forms a 3-7-micrometer hole. Therefore, pore is controllable by choosing suitably the above-mentioned large drop child's weight-mix ratio to the above-mentioned granule child in 5 / 95 - 95/5.

[0031] Moreover, to basic raw materials, the above-mentioned organic blowing agent or combustible material is added in the above-mentioned specific range. And an average pole diameter is controllable also by adjusting the addition. Therefore, an average pole diameter can be made into the still more nearly optimal magnitude.

[0032] Moreover, the above-mentioned talc used for the above-mentioned basic raw materials is Fe_2O_3. A content is 0.1 - 0.6 % of the weight. And the sum total content of impurities, such as CaO, Na_2O, and K_2O, is 0.35 or less % of the weight. Moreover, the sum total content of impurities, such as Na_2O, K_2O, etc. which are contained in the above-mentioned fused silica, is also 0.01 or less % of the weight. Therefore, the coefficient of thermal expansion of a honeycomb structure object can promote high porosity-ization while being able to make it into a very low value.

[0033] Therefore, in the above-mentioned manufacture approach in this invention, the approach of manufacturing the honeycomb structure object which was excellent the account of a top can be offered.

[0034] Moreover, Fe_2O_3 contained in the above-mentioned basic raw materials like invention of claim 4 As for an amount, it is desirable that it is 0.7 or less % of the weight. Namely, Fe_2O_3 in the above-mentioned talc Even if it limits a content to 0.1 - 0.6% of the weight, in exceeding 0.7 % of the weight in the whole basic raw materials, there is a problem that a coefficient of thermal expansion will become high.

[0035] Moreover, as combustible material added to the above-mentioned basic raw materials, carbon can be used like invention of claim 5, for example.

[0036] Moreover, as for the sum total weight of the above-mentioned talc and the above-mentioned aluminum hydroxide in the above-mentioned basic raw materials, and the above-mentioned fused silica, it is desirable like invention of claim 6 to occupy 80% or more. There is a possibility that it may become difficult to attain high porosity in less than 80% of the weight of a case.

[0037] Moreover, as for the above-mentioned large drop child's weight-mix ratio to the above-mentioned granule child in the above-mentioned aluminum hydroxide, it is especially desirable like invention of claim 7 that it is within the limits of 5 / 95 - 50/50. In this case, the honeycomb structure object which has the further excellent property can be acquired.

[0038]
[Embodiment of the Invention]
It explains using drawing 1 - drawing 3 about the honeycomb structure object concerning the example of an operation gestalt of example this invention of an operation gestalt, and its manufacture approach. It is the honeycomb structure object which uses as a principal component cordierite which chemical composition becomes from 12 - 18 % of the weight of MgO(s) SiO_2 45-55 % of the weight and aluminum2 O3 33-42% of the weight in this example. Among 25-800 degrees C Less than [0.3x10-6/degree C] and porosity are [55 - 80% and an average pole diameter] 25-40 micrometers, and the pore on the front face of a septum consists of a 5-40 micrometers stoma and a 40-100-micrometer osculum, and the coefficient of thermal expansion which can be set the honeycomb structure object whose number of the above-mentioned stomata is 5 to 40 times the number of the above-mentioned osculums Ten-kind (sample No.E1-E10) manufacture was carried out.

[0039] And while measuring the coefficient of thermal expansion, porosity, and average pole diameter of the acquired honeycomb structure object, thermal shock resistance, collection efficiency, and a pressure loss were investigated. Moreover, five kinds also of the comparison sample were prepared (sample No.C1-C5), it was doubled, and was evaluated.

[0040] First, in manufacturing the above-mentioned honeycomb structure object, the class shown in a table 1, respectively, a cordierite generation raw material, combustible material of an amount, etc. are prepared for every sample. Components, such as these raw materials, were shown in a table 2. Subsequently, the above-mentioned combustible material etc. is mixed with the basic raw materials which consist of each above-mentioned cordierite generation raw material, and the water of optimum dose is added and kneaded. Subsequently, extrusion molding is carried out with the honeycomb extruding press machine of common knowledge of the kneaded raw material, and it cuts to the desired die length.

[0041] And 80% or more of moisture is evaporated with a microwave oven, and cut ******** is dried by 80 more-degree C hot blast for 12 hours. Subsequently, the dry Plastic solid was calcinated at 1400 degrees C for 20 hours, and the honeycomb structure object was acquired.

[0042] above-mentioned sample No.E1-E10, and C1-C5 -- measurement of coefficient of thermal expansion, porosity, and an average pole diameter was performed to all honeycomb structure objects. [next,] The thermal expansion meter performed measurement of coefficient of thermal expansion. Moreover, measurement of porosity and an average pole diameter was performed in quest of pore volume with the method of mercury penetration which used the porosimeter.

[0043] The average pole diameter and porosity which were measured are shown in drawing 1 . Drawing 1 took the average pole diameter along the axis of abscissa, and took porosity along the axis of ordinate. Although sample No.E1-E10 were distributed over this invention within the limits so that it might be known from drawing 1 , either or both sides separated from C1-C5 from the above-mentioned range.

[0044] Next, the value of a coefficient of thermal expansion estimated thermal shock resistance, and when this exceeded 0.3x10-6/degree C, it was made into the rejection. Collection efficiency prepared the filter which used the above-mentioned honeycomb

structure object, and considered the case where the particulate amount which decreased by filtering exceeded 80% as acceptance. Moreover, pressure losses were engine-speed 2000 revolution per minute and a torque 100Nm service condition, and after 4-hour operation, when they were the pressure loss of 10 or less KPas, they considered 2200 cc diesel power plant as acceptance.

[0045] A result is shown in a table 2. As known in a table 2, the honeycomb structure object of sample No.E1-E10 in the manufacture approach of this invention showed the outstanding property with which are satisfied of all the three above-mentioned demand characteristics. On the other hand, the honeycomb structure object of sample No.C1-C5 did not fulfill any one demand characteristics, respectively.

[0046] That is, No.C1 is Fe 2O3. Since talc with many contents was used, the value of porosity and an average pole diameter became small, and the pressure loss became high. Since it used KARION and the alumina which are clay a total of 20% of the weight or more, having used No.C2 as basic raw materials, the value of porosity and an average pole diameter became small like No.C1, and the pressure loss became high.

[0047] Since mean particle diameter used 150 micrometers and large fused silica, an average pole diameter and coefficient of thermal expansion became large, and, as for No.C3, thermal shock resistance got worse. Since No.C4 had few additions of the organic blowing agent to basic raw materials, and an inflammable additive as 3.2 or less % of the weight, the average pole diameter became small and the pressure loss became high. On the other hand, since there were many additions of an organic blowing agent [as opposed to basic raw materials in No.C5] and an inflammable additive as 55 % of the weight, the average pole diameter became large and collection efficiency became low.

[0048] Next, the example of a measurement result of the accumulation pore volume to the pore diameter in sample No.E1 and C2 measured using the above-mentioned porosimeter is shown in drawing 2 . The honeycomb structure object (No.E1) of this invention has dramatically large accumulation pore volume compared with the conventional honeycomb structure object (No.C2), and it is clear that porosity is high so that it may be known from drawing 2 .

[0049] Next, the result of having compared the pressure loss of the above-mentioned sample No.E1 and C2 is shown. As for the honeycomb structure object (No.E1) of this invention, it turns out that pressure loss decreases about 30% compared with the conventional honeycomb structure object (No.C2) so that it may be known from drawing 3 .

[0050]
[A table 1]
（表1）

試料 No.	コージェライト生成原料 (基本原料) (質量%)					可燃性物質等 (基本原料に対する重量%)	
	タルク	溶融 シリカ	水酸化アルミニウム 小粒子：大粒子 (A)　(B)	アルミナ	カオリン	発泡剤	カーボン
E1	タルク A 38%	シリカ A 18%	50 : 50 44%	—	—	2%	20%
E2	タルク A 38%	シリカ A 18%	95 : 5 44%	—	—	↑	↑
E3	↑	↑	30 : 70 44%	—	—	↑	↑
E4	↑	↑	5 : 95 44%	—	—	↑	↑
E5	↑	↑	↑	—	—	5%	20%
E6	↑	シリカ B 18%	↑	—	—	10%	40%
E7	↑	シリカ C 18%	50 : 50 44%	—	—	2%	20%
E8	↑	↑	↑	—	—	5%	↑
E9	↑	↑	30 : 70 44%	—	—	2%	↑
E10	↑	↑	5 : 95 44%	—	—	↑	↑
C1	タルク B 39.9%	シリカ A 18%	50 : 50 42.1%	—	—	2%	20%
C2	タルク A 41.6%	シリカ A 13.7%	水酸化アルミ B 24.5%	アルミナ 10.1%	カオリン 10.1%	2%	20%
C3	タルク A 38%	シリカ D 18%	50 : 50 44%	—	—	2%	20%
C4	↑	シリカ C 18%	50 : 50 44%	—	—	0.2%	3%
C5	↑	↑	50 : 50 44%	—	—	15%	40%

[0051]

[A table 2]
（表2）　実施例にて選択した原材料の成分（wt%）

原材料名	平均粒子径	SiO$_2$	MgO	Al$_2$O$_3$	Al(OH)$_3$	Fe$_2$O$_3$	CaO+Na$_2$O+K$_2$O	LOI
タルクA	20μm	62.1	31.6	0.29	——	0.58	0.18	5.24
タルクB	20μm	62.8	30.3	0.12	——	3.00	0.09	4.94
溶融シリカ A	40μm	99.5	——	0.02	——	0.04	0.006	0.30
溶融シリカ B	30μm	99.5	——	0.02	——	0.04	0.006	0.30
溶融シリカ C	100μm	99.5	——	0.02	——	0.04	0.006	0.20
溶融シリカ D	150μm	99.5	——	0.02	——	0.04	0.006	0.20
水酸化アルミ A	1μm	0.01	——	——	99.6	0.01	0.36	34.1
水酸化アルミ B	10μm	0.01	——	——	99.8	0.01	0.16	34.2
アルミナ	1μm	0.03	——	99.4	——	——	0.09	0.30
カオリン	10μm	45.1	——	38.5	——	0.34	0.20	14.1
発泡剤	15μm	——	——	——	——	——	——	99.9
カーボン	50μm	——	——	——	——	——	——	99.9

LIO：1000℃での焼成損失

[0052]
[A table 3]
（表3）

試料No.	フィルタ特性			判定			総合判定
	熱膨張係数×10^{-7}/℃	気孔率%	平均細孔径μm	耐熱衝撃性	捕集効率	圧損	
E 1	0.15	58.0	27.0	○	○	○	○
E 2	0.15	55.2	25.5	○	○	○	○
E 3	0.16	62.0	28.2	○	○	○	○
E 4	0.18	63.6	29.0	○	○	○	○
E 5	0.22	71.0	39.6	○	○	○	○
E 6	0.23	80.0	26.0	○	○	○	○
E 7	0.28	59.5	36.1	○	○	○	○
E 8	0.28	63.1	38.1	○.	○	○	○
E 9	0.29	72.6	30.1	○	○	○	○
E10	0.29	75.0	37.5	○	○	○	○
C 1	0.19	53.9	22.2	○	○	×	×
C 2	0.20	48.3	21.3	○	○	×	×
C 3	0.32	60.6	40.2	×	○	○	×
C 4	0.28	52.0	19.4	○	○	×	×
C 5	0.29	67.1	52.0	○	×	○	×

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The explanatory view showing the relation between the average pole diameter in the example of an operation gestalt, and porosity.
[Drawing 2] The explanatory view showing the relation between the pore diameter in the example of an operation gestalt, and accumulation pore volume.
[Drawing 3] The explanatory view showing the effectiveness of the pressure loss reduction in the example of an operation gestalt.
[Drawing 4] The explanatory view showing an example of the particle size distribution of the aluminum hydroxide in this invention.
[Drawing 5] The front view of the honeycomb structure object in the conventional example.
[Drawing 6] The A-A line view sectional view of drawing 5 .
[Description of Notations]
2 ... an introductory path,
3 ... a blowdown path,
42 43 ... Lock out material,
5 ... a septum,
90 ... a honeycomb structure object,

[Translation done.]

* NOTICES *

JPO and NCIPI are not responsible for any
damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
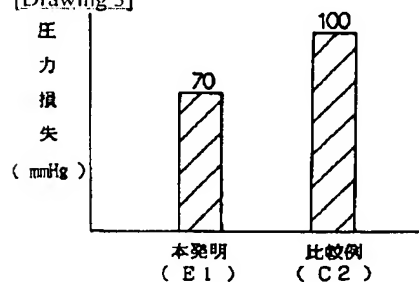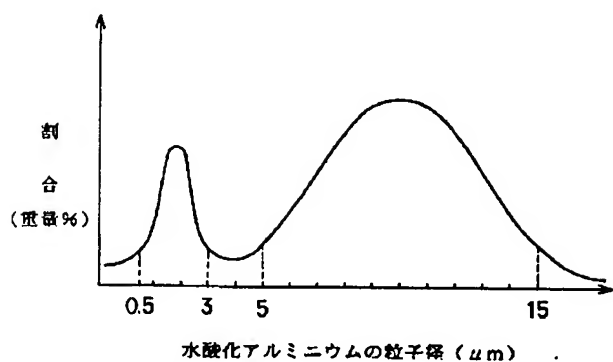3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

●：E1～E10
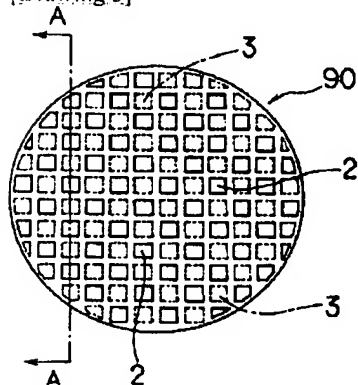○：C1～C5

[Drawing 2]

[Drawing 3]

[Drawing 4]

割合
（重量%）

0.5   3   5   15

水酸化アルミニウムの粒子径（μm）

[Drawing 5]

[Drawing 6]

排出ガス

[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number :   09-077573

(43)Date of publication of application : 25.03.1997

---

(51)Int.Cl.

C04B 38/06
B01D 39/20
B01J 21/16
B01J 35/04
C04B 35/195
F01N   3/02
// B01D 46/00

---

(21)Application number : 08-175864

(22)Date of filing :   14.06.1996

(71)Applicant : DENSO CORP

(72)Inventor : KONDO TOSHIHARU
ITO KEIJI
KAGEYAMA TERUTAKA
OBATA TAKASHI

---

(30)Priority

Priority number : 07200424   Priority date : 12.07.1995   Priority country : JP

---

(54) HONEYCOMB STRUCTURE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a cordierite honeycomb structure having such characteristics as a high rate of capture, a small pressure drop and a low coefft. of thermal expansion.

SOLUTION: This honeycomb structure is based on cordierite having a chemical structure consisting of 45-55wt.% SiO_2, 33-42wt.% Al_2O_3, and 12-18wt.% MgO and has $\leq 0.3 \times 10-6/°$ C coefft. of thermal expansion in the range of 25-800° C, 55-80% porosity and 25-40μm average pore diameter. The pores in the surfaces of the partition walls are fine pores of 5-40μm and coarse pores of 40-100μm and the number of the fine pores is 5-40 times that of the coarse pores.

LEGAL STATUS

[Date of request for examination]   04.07.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(51)Int.Cl.⁶		識別記号	庁内整理番号	F I			技術表示箇所
C 0 4 B	38/06			C 0 4 B	38/06	H	
B 0 1 D	39/20			B 0 1 D	39/20	D	
B 0 1 J	21/16			B 0 1 J	21/16	A	
	35/04	3 0 1			35/04	3 0 1 M	
						3 0 1 P	

審査請求　未請求　請求項の数7　FD　（全 9 頁）　最終頁に続く

(71)出願人　　000004260
　　　　　　　株式会社デンソー
　　　　　　　愛知県刈谷市昭和町1丁目1番地
(72)発明者　　近藤　寿治
　　　　　　　愛知県刈谷市昭和町1丁目1番地　日本電
　　　　　　　装株式会社内
(72)発明者　　伊藤　啓司
　　　　　　　愛知県刈谷市昭和町1丁目1番地　日本電
　　　　　　　装株式会社内
(72)発明者　　影山　照高
　　　　　　　愛知県刈谷市昭和町1丁目1番地　日本電
　　　　　　　装株式会社内
(74)代理人　　弁理士　高橋　祥泰

最終頁に続く

(54)【発明の名称】　ハニカム構造体及びその製造方法

(57)【要約】
【課題】　高捕集率，低圧損，かつ低熱膨張率の特性を合わせ持つコージェライトハニカム構造体及びその製造方法を提供すること。
【解決手段】　化学組成がSiO_2 45〜55重量％，Al_2O_3 33〜42重量％，MgO 12〜18重量％よりなるコージェライトを主成分とするハニカム構造体である。25〜800℃の間における熱膨張係数が0.3×10^{-6}／℃以下，気孔率が55〜80％，平均細孔径が25〜40μmであり，かつ隔壁表面の細孔は5〜40μmの小孔と40〜100μmの大孔とよりなり，上記小孔の数は上記大孔の数の5〜40倍である。

縦軸：気孔率（％）、横軸：平均細孔径（μm）
●：E1〜E10
○：C1〜C5
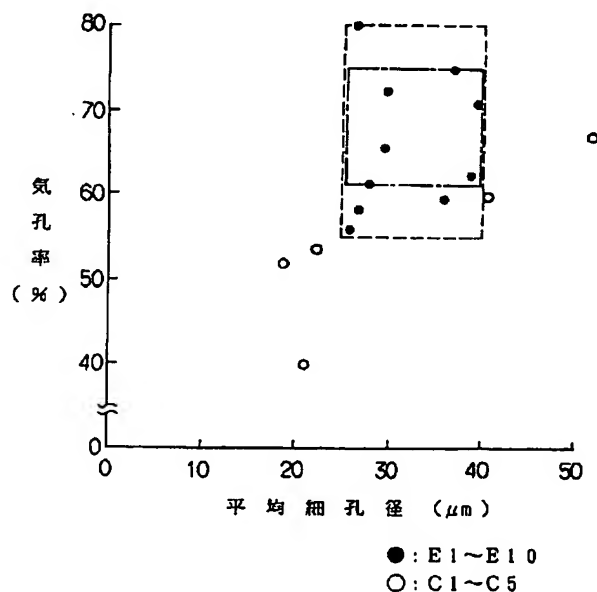
【特許請求の範囲】

【請求項１】　化学組成がSiO_2 ４５～５５重量％，Al_2O_3 ３３～４２重量％，MgO １２～１８重量％よりなるコージェライトを主成分とするハニカム構造体であって，２５～８００℃の間における熱膨張係数が０．３×10^{-6}／℃以下，気孔率が５５～８０％，平均細孔径が２５～４０μｍであり，かつ隔壁表面の細孔は５～４０μｍの小孔と４０～１００μｍの大孔とよりなり，上記小孔の数は上記大孔の数の５～４０倍であることを特徴とするハニカム構造体。

【請求項２】　請求項１において，上記気孔率は６２～７５％であることを特徴とするハニカム構造体。

【請求項３】　化学組成がSiO_2 ４５～５５重量％，Al_2O_3 ３３～４２重量％，MgO １２～１８重量％よりなるコージェライトを主成分とし，２５～８００℃の間における熱膨張係数が０．３×10^{-6}／℃以下，気孔率が５５～８０％，平均細孔径が２５～４０μｍであり，かつ隔壁表面の細孔は５～４０μｍの小孔と４０～１００μｍの大孔とよりなり，上記小孔の数は上記大孔の数の５～４０倍であるハニカム構造体を製造する方法であって，Fe_2O_3 含有量が０．１～０．６重量％，CaO，Na_2O，K_2Oの合計含有量が０．３５重量％以下であるタルクと，粒子径が０．５～３μｍの小粒子と粒子径が５～１５μｍの大粒子とが全体の５０～１００重量％を占めると共に，上記小粒子に対する上記大粒子の重量配合比が５／９５～９５／５の範囲内である水酸化アルミニウムと，平均粒子径が３０～１００μｍ，Na_2O，K_2Oの合計含有量が０．０１重量％以下の溶融シリカとを用い，上記タルクと上記水酸化アルミニウムと上記溶融シリカとの混合物を焼成した時に，化学組成がSiO_2 ４５～５５重量％，Al_2O_3 ３３～４２重量％，MgO １２～１８重量％となるように，上記タルクと上記水酸化アルミニウムと上記溶融シリカとを混合して基本原料とし，該基本原料に対して，１００℃以下で発泡する有機発泡剤，又は焼成温度よりも低い温度で燃焼する可燃性物質を合計５～５０重量％加えて混練し，次いでハニカム形状に成形後，乾燥し，次いで焼成することを特徴とするハニカム構造体の製造方法。

【請求項４】　請求項３において，上記基本原料に含有されるFe_2O_3の量は０．７重量％以下であることを特徴とするハニカム構造体の製造方法。

【請求項５】　請求項３又は４において，上記可燃性物質はカーボンであることを特徴とするハニカム構造体の製造方法。

【請求項６】　請求項３～５のいずれか１項において，上記基本原料中における，上記タルクと上記水酸化アルミニウムと上記溶融シリカの合計重量は８０％以上を占めることを特徴とするハニカム構造体の製造方法。

【請求項７】　請求項３～６のいずれか１項において，

上記水酸化アルミニウムにおける上記小粒子に対する上記大粒子の重量配合比は５／９５～５０／５０の範囲内であることを特徴とするハニカム構造体の製造方法。

【発明の詳細な説明】

【０００１】

【技術分野】本発明は，ディーゼル機関から排出されるパティキュレートを捕集するフィルタに用いるコージェライト製のハニカム構造体及びその製造方法に関する。

【０００２】

【従来技術】ディーゼル機関から排出されるパティキュレートを捕集するために，コージェライト製のハニカム構造体を用いたフィルタが利用されている。従来のハニカム構造体９０は，図５，図６に示すごとく，円柱形状であって，その長手方向に設けた多数の導入通路２及び排出通路３とを有する。

【０００３】導入通路２は，図５，図６に示すごとく，排出ガス導入側を開口しており，一方排出側を閉塞材４２によって閉塞してある。また排出通路３は，排出ガス導入側を閉塞材４３によって閉塞してあり，一方排出側を開口してある。そして，導入通路２と排出通路３とは，図５，図６に示すごとく，縦方向及び横方向に交互に，いわゆる市松模様状に配置してある。また，上記導入通路２及び排出通路３を構成する隔壁５は，多孔質であって，多数の細孔を有する。

【０００４】次に，上記従来のハニカム構造体９０を用いたフィルタによってパティキュレートを捕集する際には，図６に示すごとく，まずパティキュレートを含有した排出ガスが，上記導入通路２内に進入する。次いで，進入してきた排出ガスは，上記導入通路２の排出側が閉塞されているため，隔壁５を通過して上記排出通路３内に進入する。このとき，上記隔壁５は，排出ガス中のパティキュレートを捕獲し，排出ガスを浄化する。次いで，浄化された排出ガスは排出通路３の開口端から排出される。

【０００５】このようなハニカム構造体を用いたフィルタにおいては，パティキュレートを高い捕集効率で捕集する特性の他に，低圧損，低熱膨張率という特性が要求されている。即ち，特に重要な特性として上記３つの要求特性がある。これに対し，低熱膨張率化を狙ったものとして，例えば特開平５－２５４９５８号公報に示されたハニカム構造体がある。

【０００６】

【解決しようとする課題】しかしながら，上記従来のハニカム構造体においては，次の問題点がある。即ち，上記公報に示されたハニカム構造体は，低熱膨張率であるために耐熱衝撃性に優れ，また捕集効率も良好である。しかし，気孔率が低いため圧損を低く抑えることができない。

【０００７】また，その他の従来のハニカム構造体においても，上記３つの要求特性を全て満たすものはなく，

いずれか２つの要求特性は満足するものの残り１つの要求特性は満足しない。本発明は，かかる従来の問題点に鑑みてなされたもので，高捕集率，低圧損，かつ低熱膨張率の特性を合わせ持つハニカム構造体及びその製造方法を提供しようとするものである。

【０００８】
【課題の解決手段】請求項１の発明は，化学組成がSiO$_2$ 45〜55重量％，Al$_2$O$_3$ 33〜42重量％，MgO12〜18重量％よりなるコージェライトを主成分とするハニカム構造体であって，25〜800℃の間における熱膨張係数が0.3×10^{-6}／℃以下，気孔率が55〜80％，平均細孔径が25〜40μmであり，かつ隔壁表面の細孔は5〜40μmの小孔と40〜100μmの大孔とよりなり，上記小孔の数は上記大孔の数の5〜40倍であることを特徴とするハニカム構造体にある。

【０００９】本発明において最も注目すべきことは，上記熱膨張係数が0.3×10^{-6}／℃以下，気孔率が55〜80％，平均細孔径が25〜40μmであり，かつ隔壁表面の細孔は上記小孔の数が上記大孔の数の5〜40倍であることである。

【００１０】上記熱膨張係数が0.3×10^{-6}／℃を越える場合には，耐熱衝撃性が悪化するという問題がある。

【００１１】また，上記気孔率が55％未満の場合には，圧損が高くなるという問題があり，さらに好ましくは62％以上がよい。一方，80％を越える場合には，捕集効率が低下するという問題があり，さらに好ましくは75％以下がよい。即ち，請求項２の発明のように，上記気孔率は62〜75％であることが，さらに好ましい。

【００１２】また，上記平均細孔径が25μm未満の場合には圧損が高くなるという問題があり，一方，40μmを超える場合には捕集効率が低下するという問題がある。また，上記隔壁表面の細孔において，上記小孔の数が大孔の数の5倍よりも少ない場合には捕集開始時の初期の捕集効率が劣る。一方，40倍を越える場合には全体の捕集効率が低下すると共に製品強度が低下するという問題がある。尚，その理由の詳細は，特開昭61−129015号公報に記載した通りである。

【００１３】また，上記ハニカム構造体は，例えば円柱状の外形を有し，その長手方向に，排出ガスを導入，排出するための，隔壁によって形成される多数の通路を有する形状にすることができる。上記外形は，円柱状以外に直方体，その他の形状にすることもできる。また，上記通路の断面形状は，四角形にすることが構成上最も容易であるが，六角形，三角形，その他の形状にしても問題はない。

【００１４】次に，本発明における作用効果につき説明する。本発明のハニカム構造体は，25〜800℃の間

における熱膨張係数が0.3×10^{-6}／℃以下である。そのため，非常に優れた耐熱衝撃性を示し，急激な温度変化が繰り返し発生しても，破損することはない。

【００１５】また，気孔率が55〜80％，平均細孔径が25〜40μmであり，かつ隔壁表面の細孔は上記小孔の数が上記大孔の数の5〜40倍である。そのため，高捕集率かつ低圧損を得ることができる。

【００１６】即ち，低圧損化のためには，高気孔率化及び平均細孔径の大径化が有利であるが，本発明の構成においてはこれを十分に満足している。一方，高気孔率化及び平均細孔径の大径化を進め過ぎると捕集効率を低下させてしまうのが通常である。しかし，本発明においては，上記隔壁表面の細孔における上記特定の大きさの小孔と大孔との割合を，特定範囲内に規制している。そのため，高気孔率で，かつ平均細孔径が大径であっても，高捕集率を維持することができる。

【００１７】したがって，本発明によれば，高捕集率，低圧損，かつ低熱膨張率の特性を合わせ持つハニカム構造体を提供することができる。

【００１８】次に，上記ハニカム構造体を製造する方法としては，以下の方法がある。即ち，請求項３の発明のように，化学組成がSiO$_2$ 45〜55重量％，Al$_2$O$_3$ 33〜42重量％，MgO12〜18重量％よりなるコージェライトを主成分とし，25〜800℃の間における熱膨張係数が0.3×10^{-6}／℃以下，気孔率が55〜80％，平均細孔径が25〜40μmであり，かつ隔壁表面の細孔は5〜40μmの小孔と40〜100μmの大孔とよりなり，上記小孔の数は上記大孔の数の5〜40倍であるハニカム構造体を製造する方法であって，Fe$_2$O$_3$含有量が0.1〜0.6重量％，CaO，Na$_2$O，K$_2$Oの合計含有量が0.35重量％以下であるタルクと，粒子径が0.5〜3μmの小粒子と粒子径が5〜15μmの大粒子とが全体の50〜100重量％を占めると共に，上記小粒子に対する上記大粒子の重量配合比が5／95〜95／5の範囲内である水酸化アルミニウムと，平均粒子径が30〜100μm，Na$_2$O，K$_2$Oの合計含有量が0.01重量％以下の溶融シリカとを用い，上記タルクと上記水酸化アルミニウムと上記溶融シリカとの混合物を焼成した時に，化学組成がSiO$_2$ 45〜55重量％，Al$_2$O$_3$ 33〜42重量％，MgO12〜18重量％となるように，上記タルクと上記水酸化アルミニウムと上記溶融シリカとを混合して基本原料とし，該基本原料に対して，100℃以下で発泡する有機発泡剤，又は焼成温度よりも低い温度で燃焼する可燃性物質を合計5〜50重量％加えて混練し，次いでハニカム形状に成形後，乾燥し，次いで焼成することを特徴とするハニカム構造体の製造方法がある。

【００１９】上記製造方法において最も注目すべきことは，上記タルクと上記水酸化アルミニウムと上記溶融シ

リカとを混合して基本原料とすることである。即ち，一般的にコージェライトの原料として用いるカオリンなどの粘土類やアルミナを基本原料として使用しないことである。また，基本原料に対して，上記有機発泡剤，又は上記可燃性物質を，上記特定範囲において添加することである。

【００２０】また，上記タルクにおいて，Fe_2O_3含有量が上記限定範囲を外れた場合には以下の不具合がある。即ち，Fe_2O_3含有量が０．１重量％未満の場合には低熱膨張係数を得るための焼成温度範囲が狭くなるという問題がある。一方，０．６重量％を越える場合には熱膨張係数が大きくなると共に焼き締まりが促進されて高気孔率化が妨げられるという問題がある。また，CaO，Na_2O，K_2Oよりなる不純物の合計含有量が０．３５重量％を越える場合には，熱膨張係数が高くなるという問題がある。

【００２１】また，上記水酸化アルミニウムにおいは，粒子径が０．５〜３μmの小粒子の水酸化アルミニウムと粒子径が５〜１５μmの大粒子の水酸化アルミニウムとが，水酸化アルミニウム全体の５０〜１００％を占めている。そして，上記小粒子と上記大粒子のものが５０％よりも少なくなった場合には，所望の気孔率や熱膨張率を得ることが非常に困難になってしまう。即ち，本発明における水酸化アルミニウムの粒子径分布は，例えば，図４に示すごとく，０．５〜３μmの粒子係のものと５〜１５μmの粒子径のものが他の粒子径のものよりも多く存在していることを特徴としている。

【００２２】さらに，上記小粒子の水酸化アルミニウムと上記大粒子の水酸化アルミニウムとの重量配合比が５／９５未満の場合には，反応性が低下し熱膨張係数が大きくなるという問題があり，好ましくは５／９５以上がよい。一方，９５／５を越える場合には，細孔容積が大きくできないという問題が生じる。そのため，本発明においては，上記重量配合比が５／９５〜９５／５が良好であり，この範囲に限定している。さらには，後述するごとく，５／９５〜５０／５０の範囲が特に好ましい。

【００２３】また，上記溶融シリカにおいて，平均粒子径が３０μm未満の場合には，隔壁表面に設けられる比較的大きな孔の数が少なくなってしまうという問題がある。一方，１００μmを越える場合にはハニカム構造体の強度を低下させてしまうという問題がある。また溶融シリカに含有されるNa_2O，K_2Oよりなる不純物の合計含有量が０．０１重量％を越える場合には熱膨張係数が高くなってしまうという問題がある。

【００２４】また，上記基本原料には，１００℃以下で発泡する有機発泡剤，又は上記焼成温度よりも低い温度で燃焼する可燃性物質を加える。上記有機発泡剤，又は可燃性物質の合計添加量は，基本原料に対して，５〜５０重量％である。５重量％未満の場合には平均細孔径が小さくなりすぎるという問題がある。一方，５０重量％

を越える場合には平均細孔径が大きくなりすぎるという問題がある。

【００２５】上記有機発泡剤としては，例えば松本油脂製薬社製マイクロスフウエアーがある。また，１００℃以下で発泡することが必要な理由は，上記乾燥工程において発泡させることを目的とするからであり，乾燥工程の加熱温度に対応するものである。

【００２６】次に，上記基本原料のハニカム形状への成形方法としては，例えば上記基本原料に水等を加えて混練し，これを押出成形する方法がある。この方法によれば，ハニカム形状に押出成形後，切断することにより，容易に所望寸法のハニカム成形体を得ることができる。

【００２７】また，成形されたハニカム成形体の乾燥は，上記水分等を蒸発させるために行い，例えば約８０〜１００℃で加熱することにより行う。加熱時間は，ハニカム成形体の大きさ等に合わせて適宜選択することが好ましい。また，焼成は，従来と同様に例えば約１３００〜１５００℃の温度において５〜２０時間保持することにより行うことができる。ただし，焼成温度及び時間は，ハニカム成形体の大きさ等によって適宜変更することが好ましい。尚，上記乾燥工程と焼成工程とは，別々の工程として行ってもよいが，乾燥温度から連続的に焼成温度に変更することによって，一つの工程にまとめることもできる。

【００２８】次に，上記製造方法の作用効果につき説明する。上記ハニカム構造体の製造方法においては，上記タルク，上記水酸化アルミニウム，及び上記溶融シリカを基本原料として用い，従来のようにカオリン等の粘土類やアルミナを積極的に添加するということを行わない。そのため，従来はカオリン等の粘土類やアルミナによって比較的孔の少ない骨格部が形成されていたが，本発明においては溶融シリカや水酸化アルミニウムによって骨格部が従来よりも多孔質となる。

【００２９】即ち，水酸化アルミニウムを用いることによって，その中に含まれる結晶水が蒸発し，多数の孔が形成される。また，溶融シリカは燃焼過程で分解し，その際の体積収縮により，その部分が気孔になる。それ故，従来よりもさらに気孔率を高くすることができる。

【００３０】また，上記水酸化アルミニウムにおいては，上記小粒子が主に０．３〜０．７μmの孔を形成し，一方上記大粒子が主に３〜７μmの孔を形成する。そのため，上記小粒子に対する上記大粒子の重量配合比を５／９５〜９５／５の範囲で適宜選択することによって，細孔を制御できる。

【００３１】また，基本原料には，上記有機発泡剤又は可燃性物質を上記特定範囲において添加する。そして，その添加量を調整することによっても，平均細孔径を制御することができる。そのため，平均細孔径をさらに最適な大きさにすることができる。

【００３２】また，上記基本原料に用いる上記タルク

は，Fe_2O_3 含有量が０．１〜０．６重量％である。そして，CaO，Na_2O，K_2O 等の不純物の合計含有量が０．３５重量％以下である。また，上記溶融シリカに含有される Na_2O，K_2O 等の不純物の合計含有量も０．０１重量％以下である。そのため，ハニカム構造体の熱膨張係数は，極めて低い値にすることができると共に高気孔率化を促進することができる。

【００３３】したがって，本発明における上記製造方法においては，上記優れたハニカム構造体を製造する方法を提供することができる。

【００３４】また，請求項４の発明のように，上記基本原料に含有される Fe_2O_3 の量は０．７重量％以下であることが好ましい。即ち，上記タルク中の Fe_2O_3 含有量を０．１〜０．６重量％に限定したとしても，基本原料全体において０．７重量％を越える場合には，熱膨張係数が高くなってしまうという問題がある。

【００３５】また，請求項５の発明のように，上記基本原料に加える可燃性物質としては，例えば，カーボンを用いることができる。

【００３６】また，請求項６の発明のように，上記基本原料中における，上記タルクと上記水酸化アルミニウムと上記溶融シリカの合計重量は８０％以上を占めることが好ましい。８０重量％未満の場合には，高気孔率を達成することが困難となるおそれがある。

【００３７】また，請求項７の発明のように，上記水酸化アルミニウムにおける上記小粒子に対する上記大粒子の重量配合比は５／９５〜５０／５０の範囲内であることが，特に好ましい。この場合には，さらに優れた特性を有するハニカム構造体を得ることができる。

【００３８】
【発明の実施形態】
実施形態例
本発明の実施形態例にかかるハニカム構造体及びその製造方法につき，図１〜図３を用いて説明する。本例においては，化学組成が SiO_2 ４５〜５５重量％，Al_2O_3 ３３〜４２重量％，MgO １２〜１８重量％よりなるコージェライトを主成分とするハニカム構造体であって，２５〜８００℃の間における熱膨張係数が０．３×10^{-6}／℃以下，気孔率が５５〜８０％，平均細孔径が２５〜４０μmであり，かつ隔壁表面の細孔は５〜４０μmの小孔と４０〜１００μmの大孔とよりなり，上記小孔の数は上記大孔の数の５〜４０倍であるハニカム構造体を１０種類（試料Ｎｏ．Ｅ１〜Ｅ１０）製造した。

【００３９】そして，得られたハニカム構造体の熱膨張係数，気孔率及び平均細孔径を測定すると共に，耐熱衝撃性，捕集効率，圧損を調査した。また，その比較試料も５種類準備し（試料Ｎｏ．Ｃ１〜Ｃ５），合わせて評価した。

【００４０】まず，上記ハニカム構造体を製造するに当たっては，各試料ごとに，それぞれ表１に示した種類及

び量のコージェライト生成原料と可燃性物質等を準備する。これらの原料等の成分は表２に示した。次いで，上記各コージェライト生成原料からなる基本原料と，上記可燃性物質等とを混合し，適量の水を加えて混練する。次いで，混練した原料を周知のハニカム押出成形機にて押出成形し，所望の長さに切断する。

【００４１】そして，切断した成形体をを電子レンジにより水分の８０％以上を蒸発させ，さらに８０℃の熱風で１２時間乾燥させる。次いで，乾燥した成形体を１４００℃で２０時間焼成してハニカム構造体を得た。

【００４２】次に，上記試料Ｎｏ．Ｅ１〜Ｅ１０及びＣ１〜Ｃ５すべてのハニカム構造体に対して，熱膨張率，気孔率，平均細孔径の測定を行った。熱膨張率の測定は，熱膨張計により行った。また気孔率及び平均細孔径の測定は，ポロシメータを用いた水銀圧入法により細孔容積を求めて行った。

【００４３】測定した平均細孔径と気孔率を図１に示す。図１は，横軸に平均細孔径，縦軸に気孔率を取った。図１より知られるごとく，試料Ｎｏ．Ｅ１〜Ｅ１０は本発明範囲内に分布したが，Ｃ１〜Ｃ５はいずれか一方あるいは双方が上記範囲から外れた。

【００４４】次に，耐熱衝撃性は，熱膨張係数の値で評価し，これが０．３×10^{-6}／℃を越える場合には不合格とした。捕集効率は，上記ハニカム構造体を用いたフィルタを準備し，フィルタ通過によって減少したパティキュレート量が８０％を越えた場合を合格とした。また，圧損は，２２００ｃｃディーゼルエンジンをエンジン回転数２０００回転／分，トルク１００Ｎｍの運転条件で，４時間運転後に１０ＫＰａ以下の圧力損失であれば合格とした。

【００４５】結果を表２に示す。表２より知られるごとく，本発明の製造方法における試料Ｎｏ．Ｅ１〜Ｅ１０のハニカム構造体は，上記３つの要求特性全てを満足する優れた特性を示した。一方試料Ｎｏ．Ｃ１〜Ｃ５のハニカム構造体は，それぞれ，いずれか一つの要求特性を満たさなかった。

【００４６】即ちＮｏ．Ｃ１は，Fe_2O_3 含有量の多いタルクを使用したため，気孔率及び平均細孔径の値が小さくなり，圧損が高くなった。Ｎｏ．Ｃ２は，粘土であるカリオン及びアルミナを基本原料として合計２０重量％以上使用したため，Ｎｏ．Ｃ１と同様に気孔率及び平均細孔径の値が小さくなり，圧損が高くなった。

【００４７】Ｎｏ．Ｃ３は，平均粒径が１５０μmと大きい溶融シリカを用いたため，平均細孔径と熱膨張率が大きくなり，耐熱衝撃性が悪化した。Ｎｏ．Ｃ４は，基本原料に対する有機発泡剤と可燃性添加物の添加量が３．２重量％以下と少ないため，平均細孔径が小さくなり，圧損が高くなった。一方，Ｎｏ．Ｃ５は，基本原料に対する有機発泡剤と可燃性添加物の添加量が５５重量％と多いため，平均細孔径が大きくなり，捕集効率が低

くなった。

【００４８】次に，図２には，試料Ｎｏ．Ｅ１及びＣ２における，上記ポロシメータを用いて測定した細孔直径に対する累積細孔容積の測定結果例を示す。図２より知られるごとく，本発明のハニカム構造体（Ｎｏ．Ｅ１）は，従来のハニカム構造体（Ｎｏ．Ｃ２）に比べて累積細孔容積が非常に大きく，気孔率が高いことが明白である。

【００４９】次に，上記試料Ｎｏ．Ｅ１とＣ２との圧力損失を比較した結果を示す。図３より知られるごとく，本発明のハニカム構造体（Ｎｏ．Ｅ１）は，従来のハニカム構造体（Ｎｏ．Ｃ２）に比べて圧力損失が約３０％も減少することがわかる。

【００５０】
【表１】

（表１）

試料No.	コージェライト生成原料（基本原料）（質量%）					可燃性物質等（基本原料に対する重量%）	
	タルク	溶融シリカ	水酸化アルミニウム 小粒子:大粒子 (A):(B)	アルミナ	カオリン	発泡剤	カーボン
E1	タルクA 38%	シリカA 18%	50:50 44%	—	—	2%	20%
E2	タルクA 38%	シリカA 18%	95:5 44%	—	—	↑	↑
E3	↑	↑	30:70 44%	—	—	↑	↑
E4	↑	↑	5:95 44%	—	—	↑	↑
E5	↑	↑	↑	—	—	5%	20%
E6	↑	シリカB 18%	↑	—	—	10%	40%
E7	↑	シリカC 18%	50:50 44%	—	—	2%	20%
E8	↑	↑	↑	—	—	5%	↑
E9	↑	↑	30:70 44%	—	—	2%	↑
E10	↑	↑	5:95 44%	—	—	↑	↑
C1	タルクB 39.9%	シリカA 18%	50:50 42.1%	—	—	2%	20%
C2	タルクA 41.6%	シリカA 13.7%	水酸化アルミ B 24.5%	アルミナ 10.1%	カオリン 10.1%	2%	20%
C3	タルクA 38%	シリカD 18%	50:50 44%	—	—	2%	20%
C4	↑	シリカC 18%	50:50 44%	—	—	0.2%	3%
C5	↑	↑	50:50 44%	—	—	15%	40%

【００５１】　　　　　　　　　　　　　　　【表２】

（表2）　　実施例にて選択した原材料の成分（wt%）

原材料名	平均粒子径	SiO₂	MgO	Al₂O₃	Al(OH)₃	Fe₂O₃	CaO+Na₂O+K₂O	LOI
タルクA	20μm	62.1	31.6	0.29	——	0.58	0.18	5.24
タルクB	20μm	62.8	30.3	0.12	——	3.00	0.09	4.94
溶融シリカ A	40μm	99.5	——	0.02	——	0.04	0.006	0.30
溶融シリカ B	30μm	99.5	——	0.02	——	0.04	0.006	0.30
溶融シリカ C	100μm	99.5	——	0.02	——	0.04	0.006	0.20
溶融シリカ D	150μm	99.5	——	0.02	——	0.04	0.006	0.20
水酸化アルミ A	1μm	0.01	——	——	99.6	0.01	0.36	34.1
水酸化アルミ B	10μm	0.01	——	——	99.8	0.01	0.16	34.2
アルミナ	1μm	0.03	——	99.4	——	——	0.09	0.30
カオリン	10μm	45.1	——	38.5	——	0.34	0.20	14.1
発泡剤	15μm	——	——	——	——	——	——	99.9
カーボン	50μm	——	——	——	——	——	——	99.9

LIO：1000℃での焼成損失

【0052】　　　　　　　　　　　　　　　　　　　　　【表3】

（表3）

試料No.	フィルタ特性			判定			総合判定
	熱膨張係数 ×10⁻⁷/℃	気孔率 %	平均細孔径 μm	耐熱衝撃性	捕集効率	圧損	
E 1	0.15	58.0	27.0	○	○	○	○
E 2	0.15	55.2	25.5	○	○	○	○
E 3	0.16	62.0	28.2	○	○	○	○
E 4	0.18	63.6	29.0	○	○	○	○
E 5	0.22	71.0	39.6	○	○	○	○
E 6	0.23	80.0	26.0	○	○	○	○
E 7	0.28	59.5	36.1	○	○	○	○
E 8	0.28	63.1	38.1	○	○	○	○
E 9	0.29	72.6	30.1	○	○	○	○
E10	0.29	75.0	37.5	○	○	○	○
C 1	0.19	53.9	22.2	○	○	×	×
C 2	0.20	48.3	21.3	○	○	×	×
C 3	0.32	60.6	40.2	×	○	○	×
C 4	0.28	52.0	19.4	○	○	×	×
C 5	0.29	67.1	52.0	○	×	○	×

【図面の簡単な説明】
【図1】実施形態例における，平均細孔径と気孔率の関係を示す説明図。
【図2】実施形態例における，細孔直径と累積細孔容積の関係を示す説明図。
【図3】実施形態例における，圧力損失減少の効果を示す説明図。
【図4】本発明における水酸化アルミニウムの粒子径分布の一例を示す説明図。

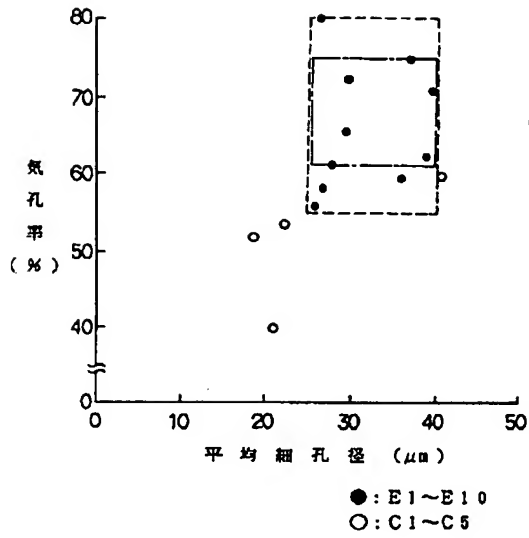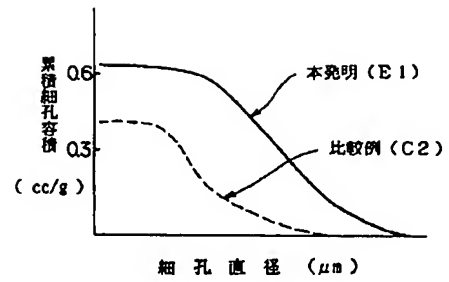【図5】従来例における，ハニカム構造体の正面図。
【図6】図5のA−A線矢視断面図。
【符号の説明】
２．．．導入通路，
３．．．排出通路，
４２，４３．．．閉塞材，
５．．．隔壁，
９０．．．ハニカム構造体，

【図1】

気孔率（％）

平均細孔径（μm）

●：E1〜E10
○：C1〜C5

【図2】

累積細孔容積（cc/g）

本発明（E1）
比較例（C2）

細孔直径（μm）

【図3】

圧力損失（mmHg）

70　　100

本発明（E1）　比較例（C2）

【図4】

割合（重量％）

0.5　3　5　　　　15

水酸化アルミニウムの粒子径（μm）

【図5】

A

3
90
2
3
2
A

【図6】

5　2　2　3　90
43
42
42
43
43
排出ガス
5　3　2
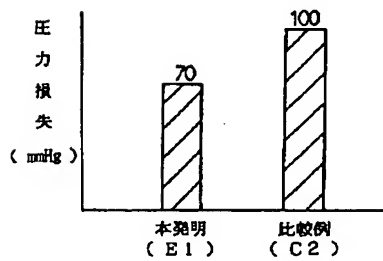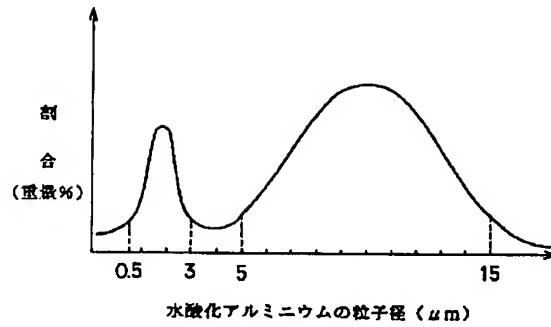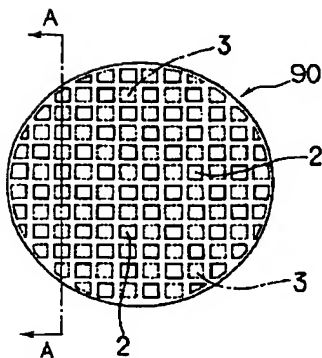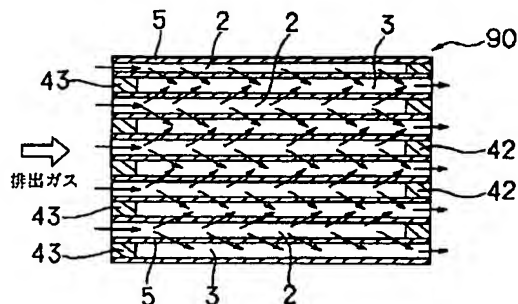
フロントページの続き

(51)Int.Cl.^{6}		識別記号	庁内整理番号	FI			技術表示箇所
C04B	35/195			F01N	3/02	301C	
F01N	3/02	301		B01D	46/00	302	
// B01D	46/00	302		C04B	35/16	A	

(72)発明者　小幡　隆
　　　　　　愛知県刈谷市昭和町1丁目1番地　日本電
　　　　　　装株式会社内